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Self-interaction in natural orbital functional theory

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Abstract

Spurious self-interaction is shown to be responsible for essentially exact H_2 potential energy curves calculated using simple one-electron density matrix functionals. For molecules with more than two electrons, bond-stretching potentials are unrealistically shallow due to overcorrelation that is most severe in the separated-atom limit. In addition, too much population is shifted into orbitals beyond the formal valence shell. Both problems are remedied by a facile self-interaction correction. At large internuclear distance, the corrected potentials are superior to those obtained from Hartree–Fock and density functional theories.

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1. Introduction

Despite its rather successful description of dynamical correlation, density functional theory (DFT) offers at best an erratic description of non-dynamical correlation arising from configurational degeneracy. Such degeneracy is unavoidable in bond breaking and in this regard contemporary DFT is unsatisfactory. Much of what passes for non-dynamical correlation in DFT is an artifact of spurious self-interaction error [1–3], while at large internuclear separation even this artifactual correlation is insufficient to overcome the inadequacies of the single-determinant Kohn–Sham (KS) formalism. Standard density functionals fail to provide qualitatively accurate global potential curves for even the simplest molecules and reactions, including H_2^+ [4], H_2 [5], and $H + H_2$ [6]. Within wavefunction quantum mechanics these are trivial problems, but accurate global description of the H_2 potential energy curve is a challenge for any method whose underlying one-electron density matrix (1-matrix) is idempotent.

Thus far, it has been an unanswered challenge, and consequently the quest for globally applicable one-electron descriptions of molecular electronic structure has broadened to include methods that employ non-idempotent 1-matrices. This is the essence of *natural orbital functional*

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theory (NOFT),[1] in which the electronic energy is expressed as a functional $E[\hat{\gamma}]$ of the 1-matrix. Equivalently, E is expressed in terms of the physical (as opposed to reference-state) natural orbitals and their (generally fractional) occupancies. A first generation of non-idempotent 1-matrix functionals [9–14] is currently being tested [14–24]. Early results are promising, especially given the simplicity of these functionals, which amount to slight modifications of the Hartree–Fock (HF) model and are based on just a few mathematical properties of the 1- and 2-matrices.

An important recent development is the merger of one such functional with KS-DFT itself [5] via the optimized effective potential formalism [25–28], a variational procedure that determines the best multiplicative potential to approximate any orbital-dependent energy functional in a standard KS calculation. Provided that the local approximation is not too severe, this may be an efficient way to accelerate the orbital-optimization bottleneck [23] in NOFT. Using an assumed form for the distribution of orbital occupancies, the first qualitatively correct (in fact, essentially exact) H_2 potential from KS theory was obtained via this KS-NOFT approach [5].

In this Letter, we first demonstrate that the quality of the aforementioned result is unique to H_2. In larger systems, spurious self-interactions lead to substantial overcorrelation that is most severe in the separated-atom limit, leading to anomalously shallow potential curves. Moreover, optimization of the orbital occupation numbers overpopulates orbitals above the Fermi level. Our second goal is to demonstrate that both problems are remedied by application of a simple self-interaction correction. We report calculations using a fully optimized, nonlocal version of NOFT, but this correction can also be applied easily within KS-NOFT. Corrected bond-stretching potentials are not as spectacular as the uncorrected H_2 result, but do offer some improvement over HF and DFT potential energy curves at large bond lengths.

2. Natural orbital functionals

A spin-restricted formalism is adopted here, wherein the natural spin-orbitals $|\varphi_i\rangle \otimes |\alpha\rangle$ and $|\varphi_i\rangle \otimes |\beta\rangle$ have identical spatial parts $|\varphi_i\rangle$ and equal occupation numbers $n_i = n_i^\alpha = n_i^\beta$, with $0 \leqslant n_i \leqslant 1$. Taking a cue from DFT, which models the 2-matrix along the adiabatic connection [29], an energy functional $E[\hat{\gamma}] = E[\{n_i\}, \{|\varphi_i\rangle\}]$ is induced by a model 2-matrix $\hat{D} = \hat{D}[\hat{\gamma}]$. For the opposite-spin component of $\hat{D}$, we use a Hartree-product:

$$D_{ij;kl}^{\alpha\beta} = \frac{1}{2} n_i n_j \delta_{ik} \delta_{jl}. \tag{1}$$

For the parallel-spin component of $\hat{D}$, the functionals of interest have the form [23]

$$D_{ij;kl}^{\alpha\alpha} = \frac{1}{2}\left[n_i n_j \delta_{ik}\delta_{jl} - f(n_i, n_j)\delta_{il}\delta_{jk}\right] \tag{2}$$

for functions f defined in Table 1.

Together, Eqs. (1) and (2) define a *reconstruction functional* $\hat{D}[\hat{\gamma}]$ for the 2-matrix. Since

$$E = \mathrm{tr}(\hat{h}\hat{\gamma}) + \mathrm{tr}(r_{12}^{-1}\hat{D}) \tag{3}$$

this reconstruction induces an energy functional [23]

$$E[\{n_k\}, \{|\varphi_k\rangle\}] = 2\sum_i n_i h_{ii} + \sum_{ij} \big(2n_i n_j \langle ij|ij\rangle - f(n_i, n_j)\langle ij|ji\rangle\big), \tag{4}$$

Table 1
Specification of 2-matrix reconstruction functionals

Functional	Refs.	$f(n_i, n_j)$
HF		$n_i n_j$
CH(ζ)	[11,13,30]	$(n_i n_j)^{\zeta/2}$
SIC-CH(ζ)	[9,10,15]	$(n_i n_j)^{\zeta/2} + (n_i^2 - n_i^\zeta)\delta_{ij}$
CHF(ζ)	[11,22]	$n_i n_j + \zeta\sqrt{\Delta_i \Delta_j}$
SIC-CHF(ζ)		$n_i n_j + \zeta\sqrt{\Delta_i \Delta_j} - \delta_{ij}\zeta\Delta_i$
MCHF(ζ)	[12]	$(n_i n_j + \zeta\sqrt{\Lambda_i \Lambda_j})/2$
SIC-MCHF(ζ)		$[n_i n_j + \zeta\sqrt{\Lambda_i \Lambda_j}$ $+\delta_{ij}(n_i^2 - \zeta\Lambda_i)]/2$

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[1] The term *density matrix functional theory* has also been suggested but is sometimes used to mean linear-scaling KS-DFT via direct optimization of an idempotent 1-matrix [7,8]. Since the natural orbitals play a key role in the present theory, the term NOFT is more descriptive.

with one- and two-electron integrals expressed in the $|\varphi_k\rangle$ basis. NOFT computations consist of minimizing this functional with respect to variations of the n_k and the $|\varphi_k\rangle$, subject to N-representability constraints on the 1-matrix [22,23].

Listed in Table 1 are the functions f that define the corrected Hartree (CH) [30,31,11,13], corrected Hartree–Fock (CHF) [11,12], and modified CHF (MCHF) [12] functionals. The quantities

$$\Delta_i = n_i(1-n_i), \quad \Lambda_i = n_i(2-n_i) \tag{5}$$

are introduced for succinctness. The CH functional adds an exchange correction to the Hartree 2-matrix $(\hat{\gamma}\otimes\hat{\gamma})/2$, although this correction does not fully annihilate self-interaction in the Hartree potential. The CHF functional corrects the HF 2-matrix $\hat{\gamma}\wedge\hat{\gamma}$. The functionals designated SIC-X result from application of a partial self-interaction correction (SIC), as detailed below. To connect with parametrizations considered previously [31, 15,16,22–24], each functional defined in Table 1 contains an adjustable parameter ζ; we restrict our attention to $\zeta = 1$.

These functionals have appeared in a variety of equivalent forms; we feel that the 'reconstructive' point of view clearly elucidates the underlying physical model, its attendant approximations, and their deficiencies, so our analysis has focused on N-representability of the reconstructed 2-matrix. (Consult Cioslowski and Pernal [15–18] for analysis of the energy functional itself.) Eqs. (1) and (2) define a model 2-matrix with a simple block structure, in which each natural spin geminal is a 2×2 determinant of natural spin orbitals, and the spectral expansion of $\hat{D}^{\alpha\alpha}$ is

$$\begin{aligned}\hat{D}^{\alpha\alpha} = {} & \sum_i d_i|\varphi_i\varphi_i\rangle\langle\varphi_i\varphi_i| \\ & + \sum_{i<j}\sum_{+,-} d_{ij}^{\pm}\big(|\varphi_i\varphi_j\rangle\langle\varphi_i\varphi_j| \pm |\varphi_i\varphi_j\rangle\langle\varphi_j\varphi_i|\big).\end{aligned} \tag{6}$$

Here $|\varphi_i\varphi_j\rangle = |\varphi_i\rangle\otimes|\varphi_j\rangle$ is a simple direct product of natural orbitals and the eigenvalues $d_i = d_i(n_i)$ and $d_{ij}^{\pm} = d_{ij}^{\pm}(n_i, n_j)$ are functions of the natural orbital occupation numbers. Antisymmetry of the 2-matrix requires that $d_i = 0$, while positivity demands that $d_{ij}^{\pm} \geqslant 0$. In contrast, for each of the functionals in Table 1 – and for all values of ζ that have been suggested to date – it follows [23] that $d_i \leqslant 0$, $d_{ij}^{+} \leqslant 0$, and $d_{ij}^{-} \geqslant 0$. (The inequalities are strict for fractional occupancies.) Each d_i represents an orbital self-interaction [9], and the SIC applied here amounts to setting each $d_i = 0$, without altering the second term in Eq. (6).

The functionals CH(1), CHF(1), and MCHF(1) each satisfy the partial trace constraint

$$\sum_k \left(D_{ik;jk}^{\alpha\alpha} + D_{ik;jk}^{\alpha\beta}\right) = \frac{1}{2}n_i(N-1)\delta_{ij}, \tag{7}$$

with $N = 2\sum_i n_i$. Removal of the d_i causes the SIC functionals to violate this constraint, so that

$$\mathrm{tr}\,\hat{D} = \frac{1}{2}N(N-1) - \Theta\sum_i \Delta_i, \tag{8}$$

where $\Theta = 4$ for SIC-MCHF(1) and $\Theta = 2$ for both SIC-CH(1) and SIC-CHF(1). The SIC 2-matrices contain fewer than $N(N-1)/2$ electron pairs, although the deviations Δ_i will be small provided that the n_i are nearly integers, as expected for closed-shell molecules. This is indeed the case for the SIC functionals but not their uncorrected counterparts (see Section 3). It is also significant that in Eq. (3) we have expressed the energy in terms of both $\hat{\gamma}$ and $\hat{D}$ rather than $\hat{D}$ alone, as these two conventions afford different energy functionals when the partial trace constraint is not satisfied. In the present formulation [Eq. (4)], any error in the partial trace of $\hat{D}$ is isolated within the electron repulsion energy.

With the exception of SIC-MCHF(ζ), each of the functionals in Table 1 has been tested for diatomic molecules [20–23], with varying success. These studies have been somewhat haphazard, however, employing either functional X or functional SIC-X, but not both. A more systematic study [14] reveals that SIC is the single most important factor that determines whether qualitatively reasonable potential curves are obtained.

3. Numerical results

In this section, we compare NOFT calculations for two molecules, H_2 and hydrogen fluoride (FH).

Table 2
Elements of the reconstructed, energy-optimized 2-matrix for H_2

Element	CH(1)		SIC-CH(1)		MCHF(1)		SIC-MCHF(1)	
	R_e	$5R_e$	R_e	$5R_e$	R_e	$5R_e$	R_e	$5R_e$
$D^{\alpha\alpha}_{1,1;1,1}$	−1.79(−2)	−1.25(−1)	0.00(+0)	0.00(+0)	−1.28(−2)	−1.25(−1)	0.00(+0)	0.00(+0)
$D^{\alpha\alpha}_{2,2;2,2}$	−9.13(−3)	−3.51(−3)	0.00(+0)	0.00(+0)	−6.89(−3)	−1.24(−1)	0.00(+0)	0.00(+0)
$D^{\alpha\alpha}_{3,3;3,3}$	−2.22(−3)	−1.89(−3)	0.00(+0)	0.00(+0)	−1.97(−3)	−3.11(−3)	0.00(+0)	0.00(+0)
$D^{\alpha\alpha}_{1,2;1,2}$	8.96(−2)	1.16(−1)	2.10(−3)	1.25(−1)	6.80(−3)	1.17(−1)	1.23(−3)	5.29(−2)
$D^{\alpha\alpha}_{1,2;2,1}$	−6.69(−1)	−2.41(−1)	−3.24(−2)	−2.50(−1)	−4.50(−2)	−2.42(−1)	−1.82(−2)	−1.45(−1)
$D^{\alpha\alpha}_{1,3;1,3}$	2.15(−3)	9.65(−4)	9.22(−4)	6.26(−5)	1.93(−3)	1.57(−3)	3.68(−4)	6.50(−4)
$D^{\alpha\alpha}_{1,3;3,1}$	−3.28(−2)	−2.20(−2)	−2.15(−2)	−5.60(−3)	−2.32(−2)	−2.50(−2)	−9.80(−3)	−1.39(−2)
$D^{\alpha\alpha}_{2,3;2,3}$	4.15(−5)	8.68(−4)	3.94(−6)	6.26(−5)	2.76(−5)	1.46(−3)	9.12(−7)	9.18(−5)
$D^{\alpha\alpha}_{2,3;3,2}$	−4.56(−3)	−2.08(−2)	−1.40(−3)	−5.59(−3)	−3.71(−3)	−2.43(−2)	−6.75(−4)	−6.61(−3)

Numbers in parentheses denote powers of 10.

Notably, H_2 is the only molecule considered by Grüning et al. [5] as a test of their combined KS-NOFT method. For reasons revealed below, very different results are obtained for H_2 than for molecules with more than two electrons, exemplified here by FH. Our H_2 calculations employ the 6-311++G(d,3p) basis, which contains three sets of p-type polarization functions and one set of diffuse sp functions on each H atom. For FH the basis is 6-31+G**. Our procedure for minimizing the functional $E[\hat{\gamma}]$, subject to N-representability constraints on $\hat{\gamma}$, has been described previously [23].

Even without any calculations it is clear that H_2 is atypical, since $\hat{D}^{\alpha\alpha}$ ought to vanish for this system, which is impossible within the ansatz of Eq. (2). In Table 2, we list a few of the largest matrix elements of $\hat{D}^{\alpha\alpha}$ for H_2. Although the vast majority of the matrix elements are minuscule, the ones shown in Table 2 are not. (Consider that $0 \leqslant D^{\alpha\alpha}_{ij;ij} \leqslant 1/2$ for the model 2-matrices considered here.) Although SIC removes only the $D^{\alpha\alpha}_{ii;ii}$ terms, the remaining matrix elements tend to be smaller than those of the uncorrected 2-matrices.

NOFT potential energy curves for H_2 are depicted in Fig. 1. Reasonable potentials are obtained from all three uncorrected functionals, including CH(1), the functional employed by Grüning et al. [5] in their KS-NOFT calculation. Those authors fit the distribution of n_i in order to replicate the full CI potential, whereas in this work both the $|\varphi_i\rangle$ and the n_i are optimized to minimize E. Interpreting this as evidence that some other (non-energy-optimized) distribution of n_i would make the CH(1) potential in Fig. 1 essentially coincident with the full CI potential, it appears that optimization of the n_i lowers the large-R part of the potential more than it lowers the region around R_e. In other words, CH(1) exhibits a greater degree of overcorrelation in the separated-atom limit, a conclusion that is bolstered by the dramatic effect of SIC on the large-R part of all the H_2 potential curves in Fig. 1. Although uncorrected functionals work well for H_2, this success is an artifact of the self-interactions d_i.

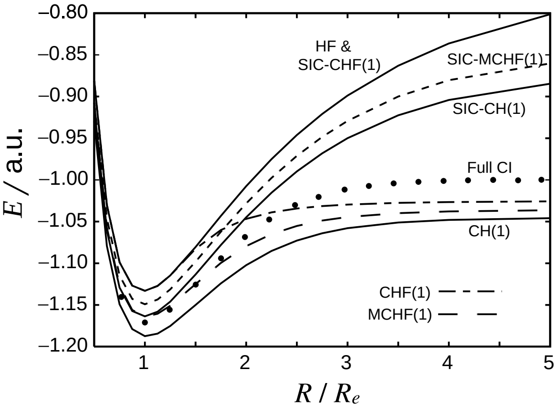

Fig. 1. H_2 potential curves.

In contrast to their behavior for H_2, uncorrected natural orbital functionals yield unrealistically shallow potential curves for other diatomic molecules [20–23,14], as illustrated for FH in Fig. 2. Comparison to the SIC results reveals the reason: spurious d_i terms lower the energy of the

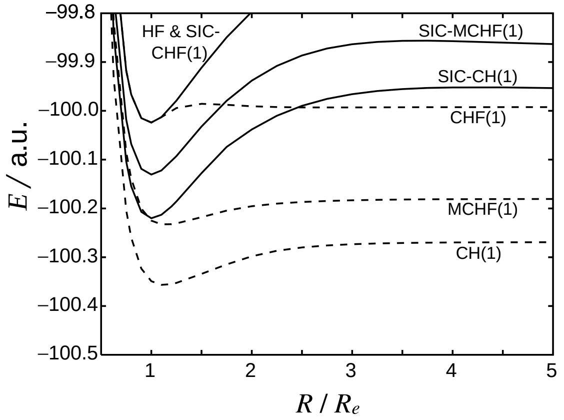

Fig. 2. FH potential energy curves from NOFT.

separated atoms to a greater extent than that of the molecule near its equilibrium geometry.

SIC potentials for FH are more reasonable, although they rise too steeply as $R \rightarrow \infty$. To put this in perspective, in Fig. 3 we compare FH potential curves from NOFT to those obtained from standard spin-restricted density functional and ab initio methods. (To facilitate comparison, the same vertical scale is used in both Fig. 2 and Fig. 3a.) Of the natural orbital functionals, SIC-CH(1) appears to provide the most accurate accounting of dynamical correlation, as evidenced by the fact the absolute energy near R_e is quite close to that obtained from correlated wavefunctions such as CCSD and CCSD(T) (Fig. 3a). Although the SIC potentials are too high in the limit $R \rightarrow \infty$, the asymptotic behavior of SIC-CH(1) and SIC-MCHF(1) is superior to that of the popular density functionals B3LYP and BPW91, which are still increasing at $R = 5R_e$. This modest improvement is something of a Pyrrhic victory, however, given the much higher computational cost of full, nonlocal NOFT relative to DFT.

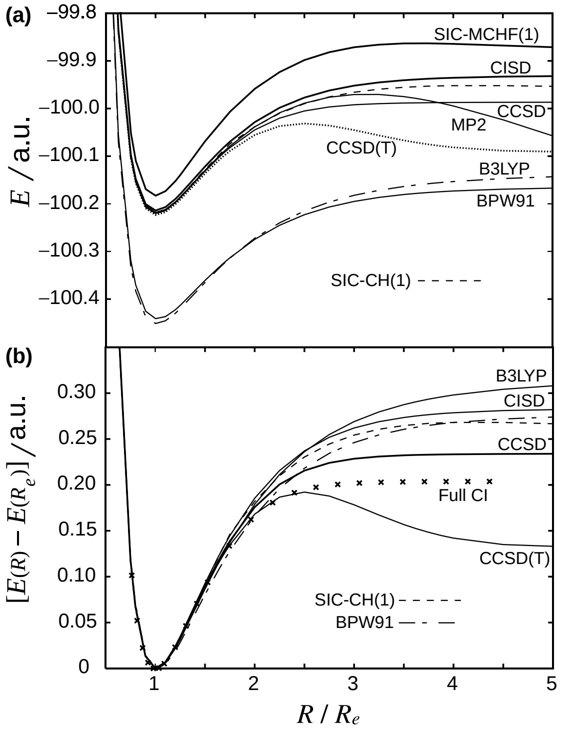

Fig. 3. (a) Absolute FH potential curves, and (b) FH potentials shifted by their respective values at $R_e = 0.9171$ Å. The 6-31+G** basis is used for each method except full CI, which uses 6-31G** [32].

The distribution of optimized occupation numbers provides additional insight into the failure of uncorrected natural orbital functionals. The largest of the n_i are listed in Table 3 for both H_2 and FH; natural orbital occupation numbers from CI wavefunctions are also tabulated. Close agreement between the CI and NOFT occupation numbers is not anticipated, but the former provide order-of-magnitude benchmarks as to what constitutes a reasonable n_i distribution. Except for SIC-MCHF(1) at large R, all of the NOFT occupancy distributions for H_2 are qualitatively reasonable.

For FH (and other diatomic molecules [14]), the same is largely true near R_e, with the exception that n_{LUMO} (occupancy of the first orbital beyond the formal valence shell) is anomalously large in CH(1) and MCHF(1). At larger values of R, each uncorrected functional shifts too much occupancy into virtual orbitals. This includes CHF(1), which converges to an idempotent 1-matrix when $R \approx R_e$. With SIC, qualitatively reasonable occupancy distributions (including n_{LUMO}) are obtained at all values of R, hence the occupancy anomaly is attributable to the d_i. In the case of SIC-CHF(1), SIC overcorrects the accretion of occupancy into virtual orbitals, leading to an idempotent solution (equal to the HF solution) even at large R, whereas

Table 3
Largest α-spin occupation numbers for H_2 and FH

Method	H_2				FH			
	Standard		SIC		Standard		SIC	
	R_e	$5R_e$	R_e	$5R_e$	R_e	$5R_e$	R_e	$5R_e$
CH(1)	0.9628	0.5082	0.9900	0.4997	1.0000	1.0000	1.0000	1.0000
	0.0186	0.4572	0.0042	0.4993	1.0000	0.8131	1.0000	1.0000
	0.0058	0.0071	0.0019	0.0002	0.9200	0.8124	1.0000	1.0000
	0.0045	0.0048	0.0013	0.0002	0.9133	0.8100	0.9515	0.6334
	0.0045	0.0038	0.0013	0.0001	0.0806	0.4815	0.0160	0.3183
	0.0005	0.0035	0.0002	0.0000	0.0177	0.0178	0.0064	0.0081
CHF(1)	1.0000	0.5005	1.0000	0.5578	1.0000	0.9870	1.0000	1.0000
	0.0000	0.4755	0.0000	0.4275	1.0000	0.8403	1.0000	1.0000
	0.0000	0.0051	0.0000	0.0035	1.0000	0.8401	1.0000	1.0000
	0.0000	0.0034	0.0000	0.0025	1.0000	0.8395	1.0000	1.0000
	0.0000	0.0026	0.0000	0.0015	0.0000	0.4799	0.0000	0.0000
MCHF(1)	0.9737	0.5037	0.9943	0.8656	1.0000	1.0000	1.0000	1.0000
	0.0140	0.4662	0.0025	0.1223	1.0000	0.8169	1.0000	1.0000
	0.0040	0.0063	0.0011	0.0033	0.9262	0.8151	1.0000	1.0000
	0.0030	0.0043	0.0007	0.0015	0.9245	0.8145	0.9706	0.5078
	0.0030	0.0033	0.0007	0.0013	0.0850	0.4933	0.0104	0.4606
	0.0006	0.0031	0.0001	0.0011	0.0143	0.0137	0.0039	0.0058
CI[a]	0.9822	0.5289			0.9950	0.9959		
	0.0100	0.4730			0.9891	0.9943		
	0.0030	0.0000			0.9891	0.9943		
	0.0022	0.0000			0.9855	0.6667		
	0.0022	0.0000			0.0115	0.3326		
	0.0001	0.0000			0.0074	0.0037		

For FH, a unit-occupied fluorine 1s orbital is omitted.

[a] Full CI for H_2 and CISD for FH.

CHF(1) is non-idempotent at large R. To a lesser extent, the other SIC functionals overcorrect in the same manner, as evidenced by HOMO and LUMO occupancies for some atoms (Table 4).

Analytic formulas [23] for the eigenvalues of $\hat{D}^{\alpha\alpha}$ help to explain the observed overcorrelation in the separated-atom limit. For the spectral expansion of $\hat{D}^{\alpha\alpha}$ in Eq. (6), we have shown [23] that the spurious negative eigenvalues d_i and d_{ij}^{+} are each associated with a natural geminal pair energy that is positive. For any fixed set of orbitals, the energy is therefore lowered by making these eigenvalues more negative, so it is instructive to determine the most negative values possible for the functions $d_i(n_i)$ and $d_{ij}^{+}(n_i, n_j)$.

The results of this exercise (Table 5) demonstrate that the most negative 2-matrix eigenvalues are obtained at half-integer occupancies, for each

Table 4
HOMO and LUMO occupation numbers for some four-electron atoms (6-31G* basis)

Method	Be	N^{3+}	Ne^{6+}
CH(1)	0.7039	0.7883	0.8199
	0.0882	0.0687	0.0599
CHF(1)	0.6305	0.7685	0.8352
	0.1173	0.0760	0.0541
MCHF(1)	0.6692	0.7717	0.8110
	0.1014	0.0745	0.0628
SIC-CH(1)	0.9609	0.9712	0.9750
	0.0101	0.0090	0.0082
SIC-CHF(1)	1.0000	1.0000	1.0000
	0.0000	0.0000	0.0000
SIC-MCHF(1)	0.9754	0.9818	0.9844
	0.0064	0.0057	0.0052
Full CI	0.9031	0.9293	0.9370
	0.0319	0.0234	0.0210

Table 5
Theoretical lower bounds on the reconstructed eigenvalues of $\hat{D}^{\alpha\alpha}$

Functional	Minimum d_i		Minimum d_{ij}^+	
	Value	Location	Value	Location
CH(1)	−0.125	$n_i = 1/2$	−0.125	$n_i = 1/4n_j$
CH(4/3)	−0.074	$n_i = 0.54$	−0.074	$n_i = 8/27n_j$
CHF(1)	−0.125	$n_i = 1/2$	−0.125	$n_i = n_j = 1/2$
CHF(1.12)	−0.140	$n_i = 0.50$	−0.140	$n_i = n_j = 1/2$
MCHF(1)	−0.125	$n_i = 1/2$	−0.125	$n_i = n_j = 1/2$

The expressions for functional X and functional SIC-X are identical, except that $d_i \equiv 0$ for the latter. CH(4/3) and CHF(1.12) have been suggested [22,24,23] as re-parametrizations of CH(1) and CHF(1).

functional examined here. (For $\zeta \neq 1$ (cf. Table 1), the lower bounds on d_i and d_{ij}^+ change markedly, but these functions still attain their minima near $n_i = n_j = 1/2$.) This provides a clue as to why these functionals are more overcorrelated for atoms. In any realistic spin-restricted model, certain of the natural occupation numbers must deviate substantially from integer values as $R \to \infty$, which is consistent with maximum overcorrelation from d_i and d_{ij}^+. In contrast, for closed-shell molecules near their equilibrium geometries, the realistic physical picture (near-integer occupancies) *competes* with overcorrelation, rather than cooperating with it, since $d_i = 0 = d_{ij}^+$ when n_i and n_j are integers.

The results of this competition are observed by tracking the most negative eigenvalue of $\hat{D}^{\alpha\alpha}$ as a function of R. For FH, the most negative eigenvalue decreases nearly monotonically as a function of R (Fig. 4a), asymptotically approaching the limiting value of −0.125. (Compared to energy calculations, tighter convergence criteria are required in order to converge the eigenvalues of $\hat{D}^{\alpha\alpha}$. Evidently the energy surface is fairly flat in the reconstructed 2-matrix.) Fig. 4b depicts $|\mathscr{R}|$ as a function of R, where $\mathscr{R}$ denotes the ratio of negative to positive-eigenvalue contributions to $E_2^{\alpha\alpha} = \mathrm{tr}(r_{12}^{-1}\,\hat{D}^{\alpha\alpha})$. In other words, $|\mathscr{R}|$ is the fraction of parallel-spin electron repulsion energy that is artificially annihilated by negative eigenvalues of $\hat{D}^{\alpha\alpha}$. (For an absolute quantification of this cancellation, see [23].) This fraction is seen to increase as a function of R, approaching a constant as $R \to \infty$. This is unambiguous evidence that anomalous features of the present functionals manifest most severely in the separated-atom limit.

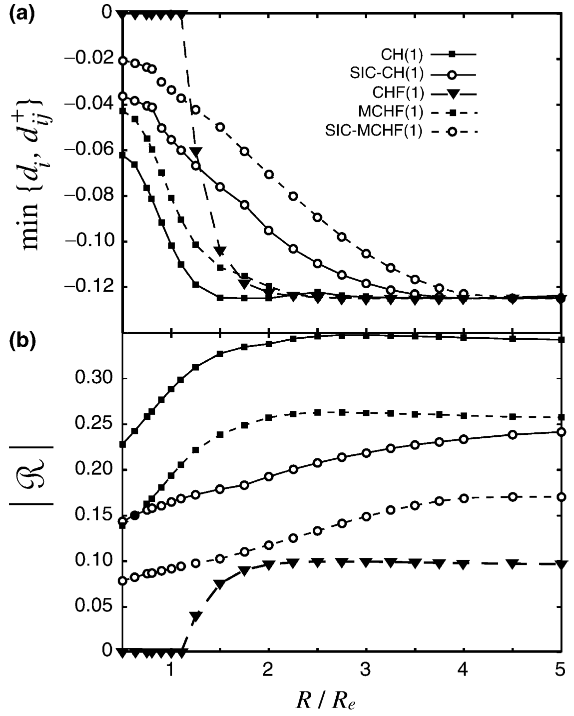

Fig. 4. For the FH molecule, (a) the most negative eigenvalue of $\hat{D}^{\alpha\alpha}$, and (b) the absolute ratio of negative to positive-eigenvalue contributions to $E_2^{\alpha\alpha}$.

4. Summary and conclusions

Our main conclusion is a disappointing one: bond-stretching potentials obtained from simple functionals of the 1-matrix are not as accurate as previous results for H_2 might insinuate. Correct asymptotic behavior for H_2 is an artifact of spurious self-interaction, the adverse effects of which are avoided only for a two-electron singlet. In this case, $\hat{D}^{\alpha\alpha}$ (and the spurious self-interaction therein) is small, though it should vanish entirely. For molecules with more than two electrons, the offending self-interactions lead to substantial overcorrelation in the separated-atom limit. A simple self-interaction correction – which, in contrast to self-interaction correction for DFT [33], does not fundamentally alter the manner in which the calculations are performed – repairs both the potential energy curve and the distribution of natural orbital occupation numbers. Notably, this correction is readily implemented within the optimized effective potential method of Grüning et al. [5], whereby the machinery of KS-DFT is put to use in NOFT.

Corrected potential curves for diatomic molecules are too steep as $R \to \infty$, although they are somewhat superior to spin-restricted density functionals in this respect. Given their remarkable simplicity, it is amazing that these natural orbital functionals perform as well as they do, and we regard this first generation of natural orbital functionals as 'proof of concept'. Relative to the tremendous intellectual capital that has driven functional development in DFT, very little effort (and no experimental data or fitting) has gone into these functionals. Insofar as decent results are obtained nonetheless, we surmise that the future of NOFT appears promising. Future development should pay mind to the role of anomalous self-interaction, recognizing furthermore that H_2 is not a sufficient test system.

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References

[1] D. Cremer, Mol. Phys. 99 (2001) 1899.
[2] V. Polo, E. Kraka, D. Cremer, Mol. Phys. 100 (2002) 1771.
[3] V. Polo, J. Gräfenstein, E. Kraka, D. Cremer, Theor. Chem. Acc. 109 (2003) 22.
[4] T. Bally, G.N. Sastry, J. Phys. Chem. A 101 (1997) 7923.
[5] M. Grüning, O.V. Gritsenko, E.J. Baerends, J. Chem. Phys. 118 (2003) 7183.
[6] D.M. Grant, P.J. Wilson, D.J. Tozer, S.C. Althorpe, Chem. Phys. Lett. 375 (2003) 162.
[7] X.-P. Li, R.W. Nunes, D. Vanderbilt, Phys. Rev. B 47 (1993) 10891.
[8] W. Yang, T.-S. Lee, J. Chem. Phys. 103 (1995) 5674.
[9] S. Goedecker, C.J. Umrigar, Phys. Rev. Lett. 81 (1998) 866.
[10] S. Goedecker, C.J. Umrigar, in: J. Cioslowski (Ed.), Many Electron Densities and Reduced Density Matrices, Plenum, New York, 2000, p. 165.
[11] G. Csányi, T.A. Arias, Phys. Rev. B 61 (2000) 7348.
[12] G. Csányi, S. Goedecker, T.A. Arias, Phys. Rev. A 65 (2002) 032510.
[13] M.A. Buijse, E.J. Baerends, Mol. Phys. 100 (2002) 401.
[14] J.M. Herbert, Ph.D. thesis, University of Wisconsin, Madison, WI, 2003. An electronic version of this document is available from the author upon request.
[15] J. Cioslowski, K. Pernal, J. Chem. Phys. 111 (1999) 3396.
[16] J. Cioslowski, K. Pernal, Phys. Rev. A 61 (2000) 034503.
[17] J. Cioslowski, P. Ziesche, K. Pernal, Phys. Rev. B 63 (2001) 205105.
[18] J. Cioslowski, K. Pernal, J. Chem. Phys. 116 (2002) 4802.
[19] J. Cioslowski, K. Pernal, J. Chem. Phys. 117 (2002) 67.
[20] A.J. Cohen, E.J. Baerends, Chem. Phys. Lett. 364 (2002) 409.
[21] V.N. Staroverov, G.E. Scuseria, J. Chem. Phys. 117 (2002) 2489.
[22] V.N. Staroverov, G.E. Scuseria, J. Chem. Phys. 117 (2002) 11107.
[23] J.M. Herbert, J.E. Harriman, J. Chem. Phys. 118 (2003) 10835.
[24] J.M. Herbert, J.E. Harriman, Int. J. Quantum Chem. 90 (2002) 355.
[25] E. Engel, R.M. Dreizler, J. Comput. Chem. 20 (1999) 31.
[26] S. Ivanov, S. Hirata, R.J. Bartlett, J. Chem. Phys. 116 (2002) 1269.
[27] S. Hamel, M.E. Casida, D.R. Salahub, J. Chem. Phys. 116 (2002) 8276.
[28] W. Yang, Q. Wu, Phys. Rev. Lett. 89 (2002) 143002.
[29] F. Colonna, D. Maynau, A. Savin, Phys. Rev. A 68 (2003) 012505.
[30] A.M.K. Müller, Phys. Lett. A 105 (1984) 446.
[31] A. Holas, Phys. Rev. A 59 (1999) 3454.
[32] A. Dutta, C.D. Sherrill, J. Chem. Phys. 118 (2003) 1610.
[33] S. Goedecker, C.J. Umrigar, Phys. Rev. A 55 (1997) 1765.